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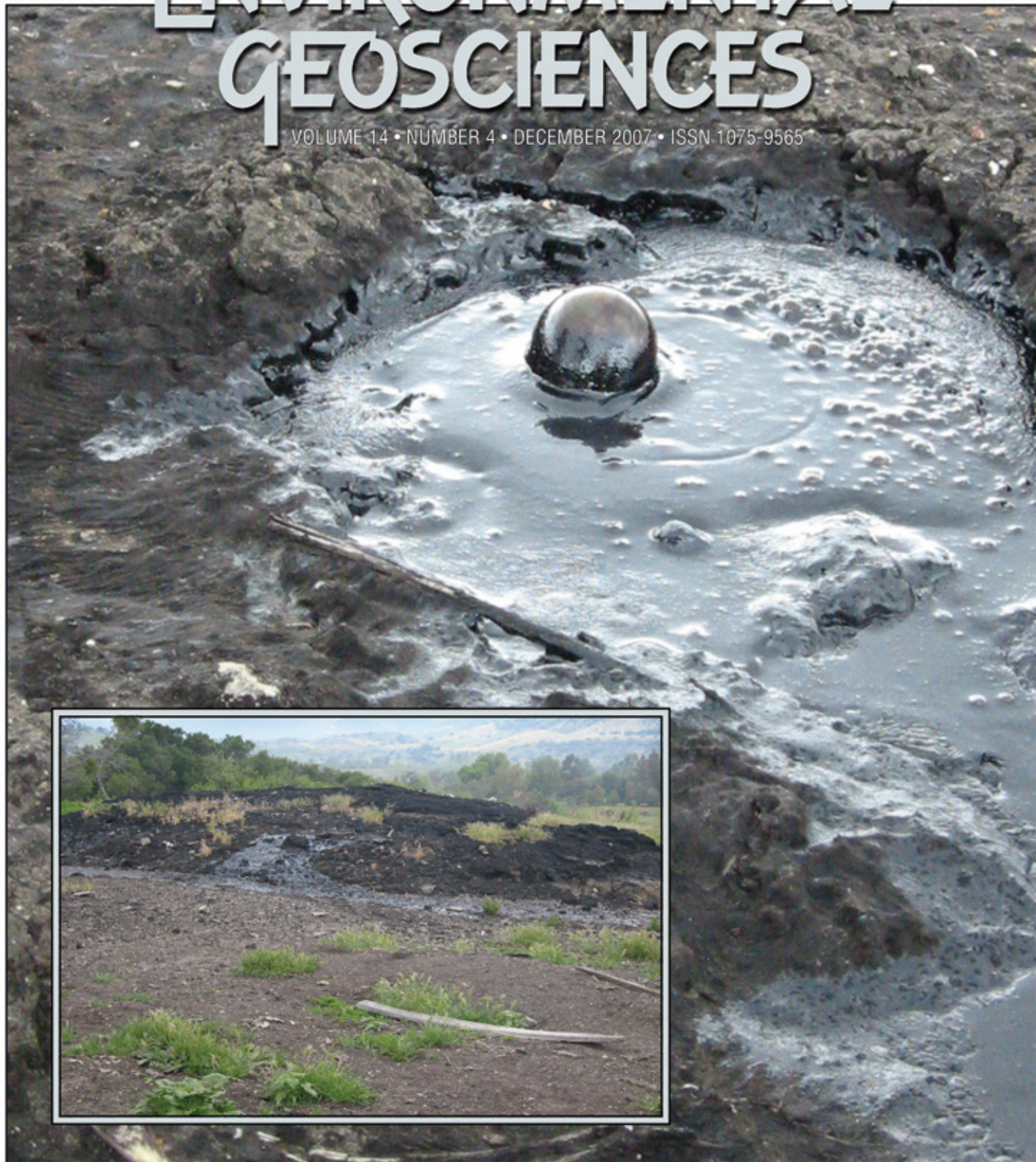Valentine, David L
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Gaseous emission rates from natural petroleum seeps in the Upper Ojai Valley, California

Marlene Duffy, Franklin S. Kinnaman, David L. Valentine, Edward A. Keller, and Jordan F. Clark

ABSTRACT

The atmospheric fluxes of methane (CH_4), carbon dioxide (CO_2), and reactive organic gases (ROGs) were determined for natural terrestrial petroleum seeps in the Upper Ojai Valley, California, by measuring the emission rates from five vents and scaling these measurements with the known distribution of seeps within the valley. The Upper Ojai Valley seeps emit about 55 m^3/day (1942 ft^3/day) of gas, of which about 15 m^3/day (529 ft^3/day; 3.6 Mg/yr) is CH_4, about 40 m^3/day (1412 ft^3/day; 27 Mg/yr) is CO_2, and less than 0.05 m^3/day (1.765 ft^3/day; 0.04 Mg/yr) are ROGs. CH_4 and ROG fluxes in the Upper Ojai Valley are, respectively, three and five orders of magnitude less than at the well-characterized Coal Oil Point field, a large offshore seep field located approximately 70 km (43 mi) to the west of the valley. The CO_2 flux from these two fields is about the same. The compositions and $\delta^{13}C$ values of seep and reservoir gases were also quantified and indicate extensive biodegradation of gaseous hydrocarbons and the input of isotopically enriched CO_2 during ascent from the reservoir. Unlike the nearby CH_4-dominated marine seeps, the largest percentage of gas emitted by seeps in the Upper Ojai Valley is CO_2.

INTRODUCTION

Natural petroleum seeps emit several gases of environmental importance, including methane (CH_4 or C_1 hydrocarbon), reactive organic gases (ROGs), and carbon dioxide (CO_2). CH_4 is approximately 25 times more effective than CO_2 as a greenhouse gas on a per-molecule basis (Lelieveld et al., 1998). Its atmospheric concentration has more than doubled during the last century as a result of anthropogenic activities, and it is the second most important gas contributing to global warming (Lelieveld et al., 1998). In addition

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to its direct function in the radiation balance of the atmosphere, by-products of its oxidation also lead to global change (Crutzen, 1991, 1995; Lelieveld et al., 1998). Most importantly, CH_4 oxidation is the principal source of stratospheric hydroxyl (OH), which contributes to ozone destruction (Crutzen, 1991).

A second set of environmentally important seep gases is ROGs, which are a family of organic gases that include propane and higher molecular weight hydrocarbons. In the presence of light, these gases react with nitrogen oxides (NO_x) in the troposphere. A by-product of these reactions is ozone (Crutzen, 1995; Jeffries, 1995), a major component of urban air pollution (i.e., smog). In some areas, such as the south coast of Santa Barbara County, natural hydrocarbon seepage can be the dominant source of ROGs (Hornafius et al., 1999).

Global estimates of the flux of hydrocarbons from natural seeps require extrapolations from limited field measurements. Using a statistical model and the known distribution of hydrocarbon deposits, Hovland et al. (1993) estimated that marine hydrocarbon seeps emit somewhere between 8 and 65 Tg/yr (1 Tg = 10^{12} g) of CH_4 to the water column. Hornafius et al. (1999) refined this estimate to 18–45 Tg/yr using a similar method. Etiope and Klusman (in press) estimated that dryland microseepage emits greater than 10 Tg/yr to the atmosphere. Recent summaries, based mainly on emissions from mud volcanoes, underwater seepage, and dryland microseepage, suggest that the geologic CH_4 contribution is 30–70 Tg/yr, equivalent to 19–44% of the total natural CH_4 source (Etiope and Klusman, 2002, in press; Etiope, 2004; Kvenvolden and Rogers, 2005).

The linkage between hydrocarbon seepage and geologic hydrocarbon accumulations is well established. In fact, the identification of seepage locations has been one of the earliest and most successful prospecting tools for hydrocarbon deposits. Production of these hydrocarbon accumulations should influence seepage rates. This is especially true when reservoir pressures are reduced below hydrostatic during production or above hydrostatic because of enhanced oil recovery techniques (e.g., Klusman, 2003a, b). Documentation of seepage rate changes as a result of production requires time series measurements that begin prior to petroleum development. These measurements rarely exist. A notable exception is the Coal Oil Point seep field, which is found about 3 km (1.8 mi) offshore from the northern coast of the Santa Barbara Channel, California. Quigley et al. (1999) documented a significant decrease in seepage area and rate after two decades near Platform Holly, the only production structure in the seep field.

Here, we quantify terrestrial hydrocarbon seepage rates in Ojai Valley, California, the birthplace of the California petroleum industry, and quantify the variations in gas composition between subsurface reservoirs and seeps. The measurements were completed near the end of the production cycle; more than 90% of the recoverable hydrocarbons have been produced from the underlying reservoirs. Because no earlier hydrocarbon seepage rates exist, the impacts of production on seepage will be evaluated by comparing our measurements to typical values observed elsewhere. These results are

important for improving estimates of the global flux of CH_4 from natural hydrocarbon seeps, which have almost certainly been effected by petroleum extraction.

Field Location and Geologic Environment

The seeps investigated in this study are located in the Upper Ojai Valley, California, near Highway 150, between Santa Paula and Ojai (Figure 1). They are found in two concentrated areas informally named the Bubbler (seeps I and II) and the Motherlode (seeps III, IV, and V) sites within the Ojai Fee oil field. These two sites contain the most active seeps in the valley and lie above large hydrocarbon reservoirs that have been producing oil and gas for about a century.

The 4.7-ha (11.6-ac) Bubbler site (34.43°N, 119.14°W) is entirely within Quaternary landslide deposits. The rocks underlying the landslide deposits are Pliocene–Pleistocene Fernando Formation and Miocene Monterey Formation. The buried Sisar and Big Canyon faults strike through the site (Figure 2). The Big Canyon fault is the likely pathway for hydrocarbon seepage because the trace of this fault is projected to be closest to the seeps at the surface (Duffy, 2004).

The parts of the Bubbler site not covered by active oil seepage or asphalt are covered by vegetation. We have identified three distinct zones of seepage, namely, from north to south, the tar mound, the asphalt drop-off, and the tar springs (seeps I and II) (Figure 2). The tar mound is a dome-shaped, 2-m (6.6-ft)-tall structure composed mostly of asphalt. Numerous small vents, which emit both gaseous and liquid hydrocarbons, cover the mound. The asphalt drop-off forms a 200-m (660-ft)-long, 1–2-m (3.3–6.6-ft)-tall ridge that runs through the center of the Bubbler site. No active vents were found along this structure. The tar springs are small ponds, which emit both gas and petroleum liquids, as well as water. Tar flows extend for more than 150 m (492 ft) downhill from each spring. Significant vegetation-free or ''kill zones'' surround each seep vent at the Bubbler site. It is unknown what causes these kill zones, but the large volume of O_2-depleted gas emitted (see below) may be a factor.

The Bubbler site lies within the North Sulphur Mountain oil field. The average depth of the hydrocarbon reservoir is approximately 1 km (0.6 mi) (California Division of Oil and Gas, 1991). As of 2001, 93% of the recoverable oil and condensate (9400 out of 10,100 million bbl) have been produced from this
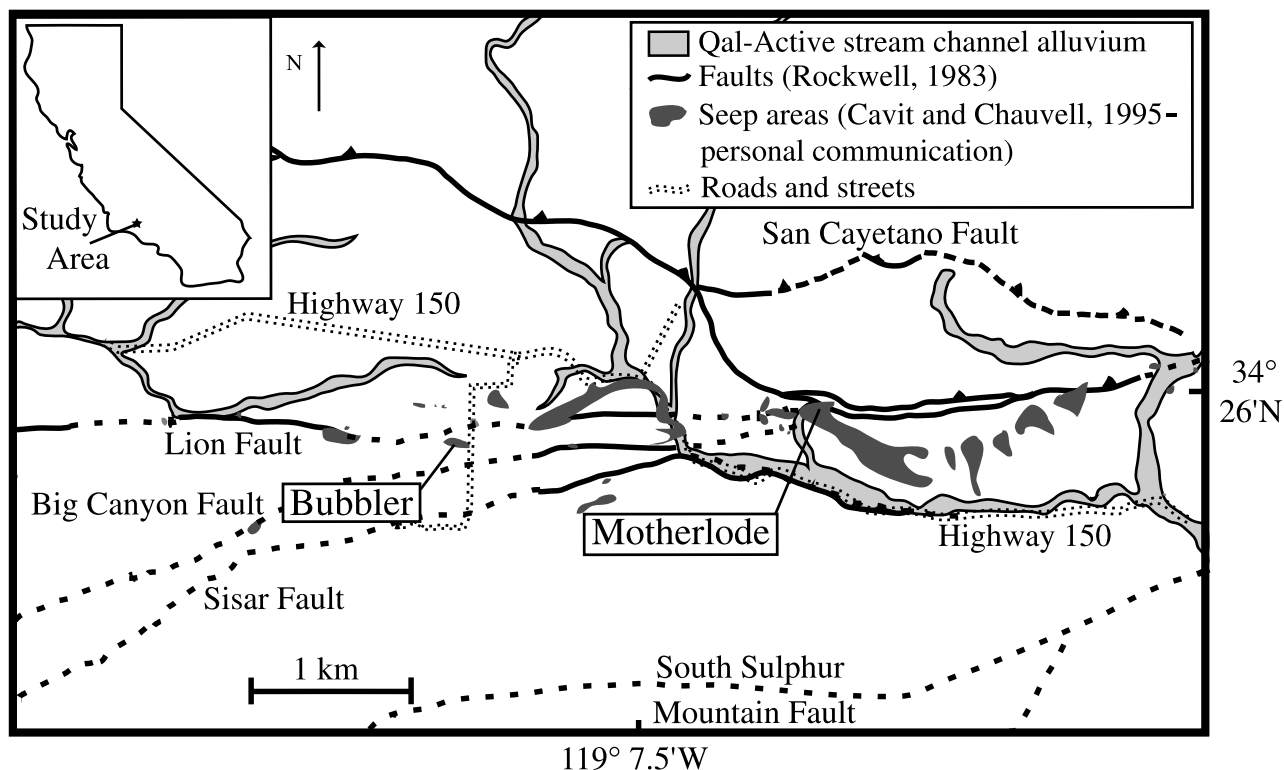
Figure 1. Map of the Upper Ojai Valley, California, showing the location of the Bubbler and Motherlode seep sites.

Figure 2. Topographic map with surface hydrocarbon features at the Bubbler site. See Figure 1 for location of the site within the Upper Ojai Valley.
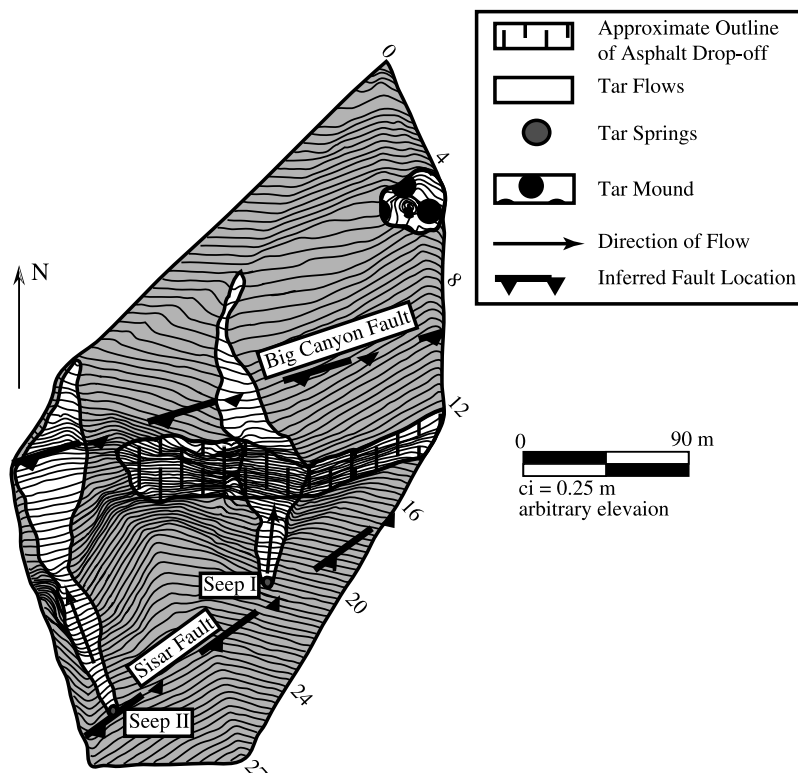
field (California Department of Conservation, 2002). Near the Bubbler site, there are two steam-injection wells used for secondary recovery of oil (California Department of Conservation, 2002). These wells have been continuously operating for more than 10 yr. The tar mound and the asphalt drop-off at the Bubbler site are both evident on all aerial photographs of the area, which are available on average of once per decade starting in 1945. However, seep I and its associated tar flow first made an appearance in a 1999 aerial photograph, and seep II along with its tar flow appeared first in a 1984 aerial photograph.

The Motherlode site (34.43°N, 119.11°W) is smaller than the Bubbler and has an area of approximately 0.4 ha (1 ac) (Figure 3). It is located in the middle of the Silverthread oil field. The San Cayetano fault runs through the site and thrusts Eocene Coldwater Formation over Miocene Monterey Formation, the hydrocarbon source and reservoir rocks (Duffy, 2004). Quaternary landslide deposits mantle a large part of the site, hampering the identification of the exact location of the fault. Cross sectional and map-view diagrams of the Motherlode site suggest that the Big Canyon fault is the likely pathway for hydrocarbons to the surface (Duffy, 2004). Nearly the entire site is covered with either natural asphalt or active seepage. The extent

of seepage on all sides of the site is evident by a significant decrease in vegetation density, although sparse vegetation manages to penetrate through older tar flows in some places.

A small, unnamed creek runs through the Motherlode site. Oil slicks form in the creek and are exported from the seep area downstream to the south. Layered asphalt deposits are exposed in the western bank of this creek (Figure 3). The exposed section is approximately 2 m (6.6 ft) high, and four asphalt layers alternate with gravelly soil layers. Radiocarbon dating of samples extracted from organic (plant) material contained within the asphalt layers suggest that petroleum has been seeping here for at least the past 20,000 yr (Duffy, 2004). These samples were carefully cleaned with organic solvents prior to processing for radiocarbon dating and should represent the age of the asphalt layer.

From initial production in the 1860s to 2001, about 18,600 million bbl of oil and condensate have been produced in the Silverthread field (California Department of Conservation, 2002). As of 2001, the estimated recoverable oil reserves in this field are 914 million bbl, indicating that more than 95% of recoverable oil has already been produced (California Department of Conservation, 2002). No secondary recovery wells exist in the area.
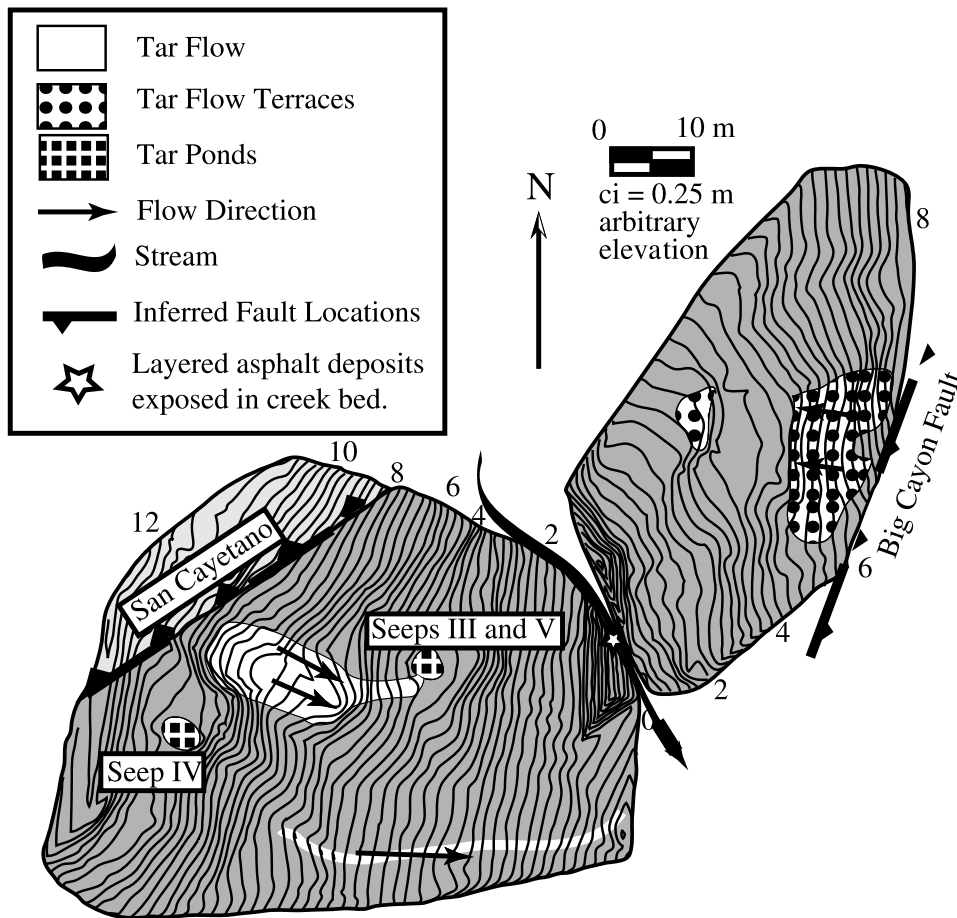
Figure 3. Topographic map with surface hydrocarbon features at the Motherlode site. See Figure 1 for location of the site within the Upper Ojai Valley.

METHODS

Detailed mapping of the sites was conducted in March 2003 using a total station. Approximately 200 points were measured at the Bubbler site and nearly 500 points were measured at the Motherlode site. These points were then downloaded into ArcView and contoured with 25-cm (10-in.) intervals for each site. Geomorphologic features were subsequently mapped onto these site maps (Figures 2, 3).

Flux Measurements

Seepage rates were determined volumetrically for 15 days in February and March 2004. Gas-capture devices (28.6-cm [11.2-in.]-diameter plastic buckets) with 0.25-in. (0.63-cm) tube outlets were placed over the seeps. Mylar balloons were attached to the outlet tube with zip ties and were allowed to partially fill with gas over a known period of time, after which, they were removed and sealed with additional ties. The balloons were only partially filled to ensure that the inside pressure did not exceed atmospheric pressure. The volume

of gas capture was determined in the laboratory by displacement, submerging the balloons in a bucket of water and recording the change in water level to the nearest 0.5 cm (0.2 in.). The measurement error corresponds to a ±0.3 L volume uncertainty. The compressibility of gas in the balloon was ignored because the calculated impact on displacement is less than 2%. At the Bubbler site, seeps I and II were not entirely covered by the gas-capture device. Therefore, the total flux was determined by multiplying the measured flux by the ratio of the total area to the collection area (10:1 for seep I and 2:1 for seep II).

Compositional Analysis

Gas samples from the four largest seeps (seep V was not sampled) were collected in pre-evacuated serum bottles on four separate occasions (Table 1). Reservoir gas was also collected in a serum bottle about 1 yr after the seep study was completed (Table 2). Before creating the vacuum, the serum bottles were flushed with He gas to remove air. Seep gases were collected using an inverted funnel in syringes and transferred through the

Table 1. Normalized Composition of Carbon Gases (Mole Percent) from the Upper Ojai Valley Seeps*

Date	Gas**	CH_4	CO_2	C_2	C_3	$n\text{-}C_4$
September 4, 2003	Seep I	25.8	74.1	0.07	0.02	<0.01
March 8, 2004	Seep I	21.2	78.1	0.08	<0.01	<0.01
March 16, 2004	Seep I	21.4	78.6	0.07	<0.01	<0.01
April 9, 2004	Seep I	22.8	77.2	0.04	<0.01	<0.01
September 4, 2003	Seep II	25.5	74.4	0.07	0.04	<0.01
September 4, 2003	Seep II	25.5	74.4	0.07	0.04	<0.01
March 8, 2004	Seep II	22.4	76.7	0.09	0.06	<0.01
March 16, 2004	Seep II	24.2	75.7	0.08	0.05	<0.01
March 16, 2004	Seep II	24.3	75.5	0.09	0.06	<0.01
April 9, 2004	Seep II	25.4	74.5	0.06	0.03	<0.01
September 4, 2003	Seep III	73.9	25.7	0.39	0.05	<0.01
March 8, 2004	Seep III	71.6	27.8	0.42	0.19	<0.01
March 16, 2004	Seep III	70.9	28.7	0.36	0.07	<0.01
March 16, 2004	Seep III	71.0	28.6	0.34	0.08	<0.01
April 9, 2004	Seep III	73.0	26.6	0.39	0.03	<0.01
April 9, 2004	Seep IV	72.5	27.2	0.28	0.07	<0.01
April 15, 2005	NSM	69.3	23.3	3.5	2.4	1.5
November 15, 2005	NSM	69.3	22.7	3.9	3.0	1.1
November 15, 2005	ST	69.5	20.8	5.3	3.3	1.2

*The standard error was ±3%.
**See Figures 2 and 3 for locations. NSM and ST refer to reservoir gas from the North Sulfur Mountain and Silverthread oil fields.

septa of the serum bottles using 22-gauge needles. Abundant components of the gas, including CO_2, C_1–C_4 hydrocarbons (methane, ethane, propane, and n-butane), nitrogen, and oxygen were quantified using gas chromatography (Agilent Technologies 3000A microthermal conductivity gas chromatograph) with 4–5-mL sample aliquots. These gases were separated on Molecular Sieve, and Plot Q capillary columns run in parallel with helium as the carrier gas. This technique has a minimum detection limit of approximately 10 ppm and a reproducibility of ±2% relative standard deviation. The detector response was calibrated with standards mixed and certified by AirLiquide, Inc.

Stable carbon isotope ratios ($^{13}C/^{12}C$) of C_1–C_4 hydrocarbons and CO_2 were measured for seep and reservoir samples by continuous flow isotope ratio mass spectrometry (IRMS). This measurement was achieved using a Delta Plus XP IRMS coupled with a Trace gas chromatograph (GC) via a GC/Combustion III interface (system components all from Thermo Finnigan,

now ThermoElectron) at the University of California–Santa Barbara Marine Science Institute's Analytical Laboratory. A 30-m × 0.32-mm (98-ft × 0.012-in.) ID CarbonPlot capillary column (Agilent Technologies) was used to separate the different gases, with helium as the carrier gas at a constant flow rate of 1.0 mL/min. The size of the injected gas sample was 10–100 μL, depending on the mixing ratio. Individual components were resolved using an isothermal temperature setting: 60°C for C_1 and CO_2, 110°C for C_2, 160°C for C_3, and 210°C for C_4. The eluent from the GC was passed into a 950°C Pt/Ni/Cu combustion reactor, in which the organic components are quantitatively converted to CO_2 before passing into the mass spectrometer. $^{13}C/^{12}C$ ratios were measured relative to CO_2 reference gas, which was calibrated against NBS19 (National Institute of Standards and Technology SRM 8544), and were expressed using the standard δ notation as per mil (‰) deviations relative to the international standard V-PDB (Peedee belemnite carbonate, as established by the International Atomic Energy Agency; Coplen, 1995).

RESULTS

Gas Flux

The emission rates of gas at the five different seeps are distinctly bimodal (Figure 4). Daily emission rates at the Bubbler site (seeps I and II) were between 5 and 75 m^3/day (176 and 2648 ft^3/day), three to four orders of magnitude greater than the rates from the three Motherlode seeps (III, IV, and V). By weight and volume, CO_2 is the most abundant gas emitted at the Bubbler site, with seep I emitting 29.9 ± 11.3 m^3/day (1055 ± 399 ft^3/day) and seep II emitting 8.0 ± 3.7 m^3/day (282 ± 130 ft^3/day). CH_4 emission is on the order of 10 m^3/day (353 ft^3/day) for the Bubbler site (seeps I and II). Seeps I and II emit on the order of 10^{-2} and 10^{-3} m^3/day (3.5 and 0.35 ft^3/day) of C_3, respectively. At the Motherlode site, CH_4 is the most abundant gas, and on the order of 1×10^{-3} m^3/day (0.35 ft^3/day) is emitted at each seep (III, IV, and V). These three seeps also each emit approximately 1×10^{-3} m^3/day (0.35 ft^3/day) of CO_2. C_3 emission at these seeps is on the order of 10^{-6} m^3/day (3.5×10^{-5} ft^3/day).

To obtain an estimate of the valley flux, the total number of seeps needs to be estimated. Exploration of the valley both through aerial photographs and ground observations determined that there are no other active seeps as large as the Bubbler seeps. However, numerous

Table 2. Carbon Isotope Ratios from the Upper Ojai Valley Seeps*

Date	Gas**	$\delta^{13}C_{C_1}$	$\delta^{13}C_{CO_2}$	$\delta^{13}C_{C_2}$	$\delta^{13}C_{C_3}$	$\delta^{13}C_{i\text{-}C_4}$	$\delta^{13}C_{n\text{-}C_4}$	$\delta^{13}C_{i\text{-}C_5}$	$\delta^{13}C_{n\text{-}C_5}$
September 4, 2003	Seep I	−45.9	23.9	−26.9	−2.4[†]				
April 9, 2004	Seep I	−46.0	23.0						
September 4, 2003	Seep II	−44.1	16.1	−28.2	−12.0	−9.7[††]	−12.5[††]	−20.0[†]	−13.9[‡]
April 9, 2004	Seep II	−47.4	15.4						
September 4, 2003	Seep III	−41.3	27.2	−28.1	−5.4	−21.8[††]	−19.5[††]		
April 9, 2004	Seep III	−41.5	26.6						
April 9, 2004	Seep IV	−41.7	25.4						
April 15, 2005	NSM	−46.7	10.3	−29.6	−27.8		−26.3		
November 15, 2005	NSM	−47.9	10.6	−30.1	−27.9	−23.6	−25.7	−20.7	−26.9
November 15, 2005	ST	−45.6	8.8	−29.2	−27.2	−26.2	−25.0	−23.8	−26.5

*See Figures 2 and 3 for locations. Standard error was ±0.2‰ for all samples, unless otherwise noted.

**See Figures 2 and 3 for locations. NSM and ST refer to reservoir gas from the North Sulfur Mountain and Silverthread oil fields.

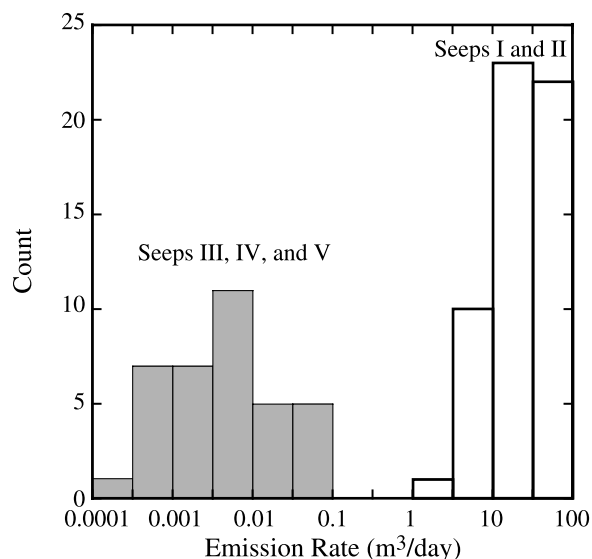[†]Error for these samples was ±1.6‰.

[††]Error for these samples was ±1.7‰.

[‡]Error for these samples was ±1.3‰.

seeps as large as or smaller than the Motherlode seeps were found. The location and size of the few seeps surveyed outside of the Bubbler and Motherlode sites agreed well with a catalog of seep characteristics (e.g., single or multiple vents, relative emission rate, etc.) and locations prepared by Hodgson (1980). Hence, this catalog is the primary data used to extrapolate the mea-

Figure 4. The distribution of seepage emission rates observed in February and March 2004 in Ojai Valley.

sured fluxes. In Hodgson's catalog, the Motherlode site is described as having multiple flows. It was assumed for simplicity that every site described has multiple flows contained in three small seeps. All other sites were assumed to have a single seep. A total of 27 multiple flow and 22 small seeps were catalogued in Hodgson's report. Therefore, we estimate that there are, presently, 103 small seeps active in the Upper Ojai Valley and two large seeps at the Bubbler site.

To estimate the total valley flux, the average flux from seeps III, IV, and V was multiplied by the estimated number of small seeps and added to the flux from seeps I and II. The gas composition of the 103 small seeps was assumed to be the average composition measured at the Motherlode site. The sites selected for field measurements in this study are the most profuse seeps in the area. Thus, extrapolation from these sources would tend to overestimate the point source emissions for the whole valley.

The average total emission rate of seep gas from III, IV, and V is about 1.2×10^{-2} m^3/day (0.42 ft^3/day). Therefore, total seepage in the Upper Ojai Valley, without the Bubbler seeps, is approximately 1 m^3/day (35 ft^3/day). When added to the two seeps at the Bubbler, the total volume of gas seeped into the valley is about 39 ± 15 m^3/day (1377 ± 529 ft^3/day). The contribution of seeps I and II is, on average, 95% of the total valley flux.

CH$_4$ emitted from all the smaller seeps in the valley is approximately 0.8 m^3/day (28 ft^3/day), leading to a mean valley CH$_4$ emission rate of less than 15.0 m^3/day (529.0 ft^3/day) (9–21 m^3/day; 317–741 ft^3/day) once the Bubbler seeps are included. CH$_4$ emission at seeps I and II make up 87% of the total valley CH$_4$ flux. ROGs are a very small percentage of the total gas flux. The whole valley emits between 0.02 and 0.05 m^3/day (0.70 and 1.76 ft^3/day) of ROGs. In this study, the only ROG measured is C$_3$; thus, our estimate is a minimum.

Variations in Gas Composition

Gas samples (Table 1) were collected in three different months at different times of day and display only slight temporal variability. CO$_2$ was found to account for 70–77% of the total emissions at the two Bubbler seeps (I and II), compared with 27% of the total emissions at the Motherlode site. CH$_4$ makes up the bulk of the remaining gas at both the Bubbler and Motherlode seeps, about 23 and about 72%, respectively. C$_2$–C$_3$ hydrocarbons account for less than 1% of gas emitted at each of the seeps, and higher hydrocarbon gases (such as C$_4$) are below our detection limit of 10 ppmv. The average carbon isotope compositions of the CH$_4$, δ^{13}C = −46‰ at the Bubbler seeps and δ^{13}C = −41‰ at the Motherlode seeps, are typical of hydrocarbon reservoirs containing thermogenic gas (Bernard et al., 1976; Hunt, 1996). The ratio of CH$_4$/(C$_2$ + C$_3$) varied between 100 and 300 and is between typical values associated with thermogenic and bacterial-derived hydrocarbon gases (Bernard et al., 1976; Hunt, 1996), although the ratio is closer to the thermogenic end member.

Gas samples from the North Sulfur Mountain and Silverthread reservoirs were similar (Table 2). The reservoir gas is composed of primarily CH$_4$ ($\sim$67%) and CO$_2$ ($\sim$24%). The ratio of CH$_4$/(C$_2$ + C$_3$) and the carbon isotope composition of the CH$_4$ indicate that the gas is thermogenic. Significant compositional differences are apparent between the reservoir and the overlying seeps. The seeps, especially at the Bubbler site, contain abundant CO$_2$ and have higher CH$_4$/(C$_2$ + C$_3$) ratios. The δ^{13}C of C$_1$–C$_5$ hydrocarbons is enriched in the seep gas relative to the reservoir gas (Tables 1, 2). CH$_4$ and C$_2$ display the smallest average shifts, $\sim$+2‰, whereas C$_3$ and C$_4$ hydrocarbons exhibit much larger shifts, which average +18.9 and +9.7‰, respectively. The average CO$_2$ shift between the reservoir and seep gas is also marked by a δ^{13}C enrichment of +12.6‰.

DISCUSSION

Several key assumptions impact estimates of whole valley gas emission rates. Although there are multiple locations in the valley that have liquid hydrocarbon seepage that do not show visible signs of gaseous emissions, such as bubbling, all catalogued seeps are assumed to emit gas. Furthermore, the seep catalog of Hodgson (1980) is assumed to be complete. The system is clearly dynamic as shown by the appearance of seeps I and II in the last few decades, and thus, extrapolating with a 25-yr-old survey introduces uncertainty. However, the collective flux of the smaller point source seeps makes a very small contribution to the whole valley, so a difference in the total number of small seeps or the size of the seeps will not alter the total estimate beyond the range of the measurement uncertainty.

Another assumption involved in making the whole valley estimate is that there are no other seeps of the same scale as seeps I and II. If there were another seep of this magnitude, it would have a significant impact on the total seepage of the valley. The most likely locations for large seeps are along faults. A lack of evidence for large seeps from field exploration of the valley and examination of recent aerial photographs makes the existence of other large seeps unlikely.

The last assumption is that the gas composition of the catalogued seeps in the valley is the same as seeps III, IV, and V. The assumption is unlikely to make a difference in the estimated valley flux because seeps I and II account for 87% of CH$_4$, greater than 95% of CO$_2$, and 79% of ROGs emitted. Thus, a small difference in the composition of the gases emitted by the small seeps would not make a significant difference in the total volume of CH$_4$ or ROGs emitted.

Upper Ojai Emissions to the Atmosphere

The absolute volume of gases emitted by the seeps is less important than how this volume compares with other seep areas. Etiope and Klusman (2002) estimated that individual mud volcanoes emit up to 10^3 t/yr (5 × 10^8 m^3/yr; 1.76 × 10^{10} ft^3/yr), localized hydrocarbon flows and vents emit 10^2 t/yr (5 × 10^7 m^3/yr; 1.76 × 10^9 ft^3/yr), and microseepage emits 1–100 mg/m^2/day. None of the individual seep vents in the Upper Ojai Valley emit as much gas as the examples cited by Etiope and Klusman (2002). Seep I emits the most CH$_4$ per year, but at 2.7 t/yr, it is still an order of magnitude smaller than the Etiope and Klusman definition of

localized hydrocarbon flows. At 0.008 t/yr, the smallest of the measured seeps (seep III) emits four orders of magnitude less CH_4 than the cited localized hydrocarbon flows; however, at 3.4×10^4 mg/m^2/day, the rate is still two orders of magnitude greater than the rate of Etiope and Klusman's microseepage.

The Upper Ojai Valley seeps emit much less gas than the well-characterized Coal Oil Point seep field, which lies approximately 70 km (43 mi) west in the Santa Barbara Channel. Total area, total number of seeps, and intensity of seepage are orders of magnitude less in the Ojai Valley. For instance, the largest seeps at Coal Oil Point emit between 2000 and 4500 m^3/day (70,629 and 158,916 ft^3/day) (480 and 1100 t/yr) of gas to the atmosphere (Washburn et al., 2005), two orders of magnitude greater than the largest valley seep and in agreement with Etiope and Klusman (2002) classification. The sea-floor composition of the offshore seeps differs from the Ojai seeps in that they contain higher fractions of C_1–C_4 hydrocarbons and less CO_2 (Clark et al., 2003). Because the ocean is able to absorb most of the sea-floor CO_2 emissions, the atmospheric flux of CO_2 from these two fields is approximately the same.

Direct emissions of ROGs were relatively low in the Upper Ojai Valley and were estimated to be about 0.2 m^3/day (7.0 ft^3/day) or approximately 0.01 t/yr. This value is small in comparison to the approximately 12,000 t/yr of ROGs emitted at the Coal Oil Point seeps (Hornafius et al., 1999). The annual anthropogenic ROG emissions in Ventura County are about 22,000 t, with the largest contributions, approximately 12,000 t/yr, coming from mobile sources (Ventura County Air Resources Board, 2007). In comparison to the total emissions for Ventura County, the Upper Ojai Valley seeps are not a significant source of ROGs. However, it is important to note that our estimate is only for direct gaseous emissions. They do not include the flux from the volatilization of the emitted oil, which may be a significant ROG source locally.

Subsurface Processes Impacting Gas Composition

Despite similar compositions for reservoir gas, seepage at Coal Oil Point contains about 35 times more ROGs per volume of CH_4 relative to Upper Ojai Valley seepage (F. Kinnaman and D. Valentine, 2003, unpublished data). A plausible explanation for the lack of ROGs in Upper Ojai Valley seep gas is subsurface biodegradation during gas ascent from the reservoir. A comparison of reservoir gas to associated surface seepage supports this

hypothesis. In the case of the Motherlode and Silverthread site (seeps III, IV, and V), the CH_4-to-CO_2 ratio decreases from 3.34 to about 2.6 between the reservoir and the seeps, whereas the relative proportions of C_2–C_4 hydrocarbons (to either CH_4 or CO_2) decrease by more than an order of magnitude. Enrichments in $\delta^{13}C$ of the C_1–C_4 components of natural gas have been previously used as indicators of oxidation in the deep subsurface (James and Burns, 1984; Pallasser, 2000; Boreham et al., 2001). Such biological activity is the simplest explanation for the observed isotopic enrichments in all of the seep gas hydrocarbons (Table 2) and is consistent with results from microbial enrichment cultures (Kinnaman et al., 2007). The $\delta^{13}C$ enrichments between reservoir and seep gas hydrocarbons suggest that C_3, n-C_4, and n-C_5 are preferred substrates and are significantly oxidized in the subsurface. This assumption is confirmed by the low concentrations of ROGs in the seep gas. However, the observed isotopic enrichment of approximately 13‰ in CO_2 over this same interval is not consistent with this interpretation for reasons of isotopic mass balance.

Differences in composition between reservoir and seep gas at the Bubbler and North Sulfur Mountain site are more extreme than at the Motherlode and Silverthread site; an order of magnitude change exists in the average CH_4-to-CO_2 ratio between the reservoir (3.0) and the two surface seeps (0.30 at seep I and 0.33 at seep II). As with the Bubbler and North Sulfur Mountain site, there is a trend toward isotopic enrichment in the C_1–C_4 hydrocarbons, which can be explained by subsurface hydrocarbon oxidation mediated by microbes. However, the observed isotopic enrichment of CO_2 in the seep gas relative to reservoir (4.8–13.6‰) and the ten-fold increase in CO_2 relative to CH_4 dictate a source of ^{13}C-enriched CO_2 feeding the seeps.

Records of the North Sulfur Mountain and Silverthread oil fields (California Division of Oil and Gas, 1991) indicate two subsurface reservoirs connected vertically by faulting with oil-field waters of approximately one-third the salinity of seawater. This freshwater input and the extensive faulting provide a potential source of oxidants to the subsurface. Microbially mediated reactions converting hydrocarbons to methane, CO_2, and biomass have been noted in sulfate-limited conditions (Zengler et al., 1999). Methanogenesis via CO_2 reduction at intermediate depths may further enrich the residual CO_2 in ^{13}C during its transport. The introduction of oxidants into the subsurface could also drive processes such as sulfide or ferrous iron oxidation, with the net effect being the production of acid. This will act

to degas alkaline fluids and dissolve carbonate minerals, thus altering CO_2 levels significantly. The Monterey Formation is known to harbor ^{13}C-enriched carbonates (Murata et al., 1967; Pisciotto, 1981), although not as enriched as the CO_2 observed in the seep gases.

At the Bubbler and North Sulfur Mountain site, it is tempting to relate the high CO_2 levels with the nearby steam injection wells. The operational details and history of these wells are not available to us, but several mechanisms are possible. The most direct impact of these wells would be the direct injection of CO_2 back into the subsurface, although this does not satisfactorily explain the isotopic composition of the seep gas. The direct injection of oxidants into the subsurface might also impact seep gas composition in ways discussed above. Water-rock reactions during the steam flood could favor the abiogenic formation of hydrocarbons via Fischer-Tropsch reactions, a process first described at hydrothermal settings (Welhan and Craig, 1979) and considered as a minor source of hydrocarbons in petroleum systems (Sherwood-Lollar et al., 2002). As with methanogenesis, these processes use CO_2 as a reactant and leave the residual CO_2 isotopically enriched. The key evidence for this process is absent in the gas component isotopic distributions, which display the classic progressive enrichments in C_1–C_4 seen in thermogenic petroleum settings. The aforementioned microbial oxidation could have eroded this signal, however.

Potential Impact of Oil and Gas Production on Seepage

The long history of oil production in the area is likely one of the reasons for the relatively small volume of observed seepage. Offshore Coal Oil Point, oil production has decreased seepage by as much as 50% over an approximately 20-yr period near the production area (Quigley et al., 1999). There has been oil production in the Upper Ojai Valley for nearly 150 yr. The depletion of the reservoirs is likely responsible for some of the low emission rates of the seeps and may have also impacted the chemical composition of seep gas. The influx of oxidants into the reservoir through natural faults and anthropogenic activities may also affect seepage rates. Modern oil recovery procedures include the injection of retrieved reservoir-associated water into the reservoir. Potentially exposed to the atmosphere, this water may have enhanced levels of oxidants (such as dissolved O_2, NO_3^-, or SO_4^{2-}). Microbial hydrocarbon degradation in the deep subsurface is expected to be favored by the oxidant additions of these injections, and oxidation of gaseous hydrocarbons and oil may

result. Whether this oxidation could cause a substantial decrease in the amount of seepage is uncertain, but the Bubbler sites are distinguished by anomalously high CO_2 content and are also closest to the water and steam injection sites. Because records of seepage rates have not been previously kept in this area, this hypothesis is difficult to test. Nevertheless, it would account for the relatively low emissions rates.

SUMMARY

CO_2 is the largest component of the gas emitted by natural petroleum seeps in the Upper Ojai Valley. The emission of CH_4 by the Upper Ojai Valley is about 15 m^3/day (529 ft^3/day) and is not consistent with the seepage rates categorized by Etiope and Klusman (2002). The Upper Ojai Valley seeps emit less than 0.03 m^3/day (1.05 ft^3/day) of ROGs and are not a significant source of ROGs to the local air. Both of these values should be considered minimums because dry land microseepage, which can be a large source of CH_4 and other hydrocarbons to the atmosphere (e.g., Etiope and Klusman, in press), have not been measured. Substantial differences in gas composition and carbon isotope ratios were apparent between the reservoir and seep gas. The Upper Ojai Valley is likely representative of the emission rates from terrestrial hydrocarbon seepage heavily impacted by local hydrocarbon production.

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